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(54) SYSTEM FOR NOX REDUCTION IN EXHAUST GASES

VORRICHTUNG ZUR REDUKTION VON NOX IN ABGASEN

SYSTEME DE REDUCTION DE NOX DANS DES GAZ D'ECHAPPEMENT

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Description

[0001] The present invention concerns improvements in selective catalytic reduction of NO_x in waste gas streams such as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

[0002] EP 0 758 713 (Toyota) describes a method for purifying the exhaust gas of a diesel engine which uses a catalyst to convert NO in the exhaust gas to NO₂, thereafter trapping particulate in a filter and oxidising the particulate by reaction with the NO₂. The exhaust gas is thereafter fed to a NO_x absorbent or, in one embodiment, to a NO_x conversion catalyst. Unburnt hydrocarbons and CO in the exhaust gas are trapped in a zeolite and released to react with NO_x on the NO_x conversion catalyst.

[0003] The technique named SCR (Selective Catalytic Reduction) is well established for industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NO_x content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH₃ to NO_x during higher temperature operation. We believe that SCR systems have been proposed for NO_x reduction for vehicle engine exhausts, especially large or heavy duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

[0004] We believe that if there could be a significant improvement in performance of SCR systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NO_x in a SCR system, and to improve the control of other pollutants using a SCR system.

[0005] Accordingly, the present invention provides an improved SCR catalyst system for treating combustion exhaust gas containing NO_x and particulates, comprising in combination and in order, an oxidation catalyst effective to convert at least a portion of NO to NO₂ and enhance the NO₂ content of the exhaust gas, a particulate filter, a source of reductant fluid, injection means for said reductant fluid located downstream of said particulate trap and an SCR catalyst.

[0006] The invention further provides an improved method of reducing pollutants, including particulates and NO_x in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO₂, and enhance the NO₂ content of the gas stream, removing at least a portion of said particulates in a particulate trap, reacting trapped particulate with NO₂, adding reductant fluid to the gas stream to form a gas mixture downstream of said trap, and passing the

gas mixture over an SCR catalyst.

[0007] Although the present invention provides, at least in its preferred embodiments, the opportunity to reduce very significantly the NO_x emissions from the lean (high in oxygen) exhaust gases from diesel and similar engines, it is to be noted that the invention also permits very good reductions in the levels of other regulated pollutants, especially hydrocarbons and particulates.

[0008] The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, eg truck or bus engines, but is not to be regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

[0009] We have surprisingly found that a "pre-oxidising" step, which is not generally considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NO_x to N₂ by the SCR system. We also believe that minimising the levels of hydrocarbons in the gases may assist in the conversion of NO to NO₂. This may be achieved catalytically and/or by engine design or management. Desirably, the NO₂/NO ratio is adjusted according to the present invention to the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition metal/zeolite SCR catalyst it is desirable to convert all NO to NO₂, whereas for a rare earth-based SCR catalyst, a high ratio is desirable providing there is some NO, and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NO₂. Even more surprisingly, the incorporation of a particulate filter permits still higher conversions of NO_x.

[0010] The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal throughflow honeycomb support is particularly suitable. Suitable catalysts are e.g. Pt/Al₂O₃ catalysts, containing 1-150g Pt/ft³ (0.035-5.3g Pt/litre) catalyst volume depending on the NO₂/NO ratio required. Such catalysts may contain other components providing there is a beneficial effect or at least no significant adverse effect.

[0011] The source of reductant fluid conveniently uses existing technology to inject fluid into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH₃, which was injected through an annular injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of compressed air was also injected around the nozzle; this provided

good mixing and cooling.

[0012] The reductant fluid is suitably NH_3 , but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is a less selective reductant than NH_3 and is presently not preferred.

[0013] Suitable SCR catalysts are available in the art and include Cu-based and vanadia-based catalysts. A preferred catalyst at present is a $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalyst, supported on a honeycomb through-flow support. Although such a catalyst has shown good performance in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines, which are almost exclusively turbocharged, can produce exhaust gases at greater than 500°C under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation. In one embodiment of the invention, therefore, cooling means is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilising the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends to reduce NO_x conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from 160°C to 450°C .

[0014] We believe that in its presently preferred embodiments, the present invention may depend upon an incomplete conversion of NO to NO_2 . Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of NO to NO_2 of from about 4:1 to about 1:3 by vol, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO_2 ratios. We do not believe that it has previously been suggested to adjust the NO/NO_2 ratio in order to improve NO_x reduction.

[0015] The present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by "combustion" at relatively low temperatures in the presence of NO_2 . In effect, the incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst simultaneously reducing a proportion of the NO_x . Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters, generally manufactured from a ceramic, but other designs

of particulate trap, including woven, knitted or non-woven heat-resistant fabrics, may be used.

[0016] It may be desirable to incorporate a clean-up catalyst downstream of the SCR catalyst, to remove any NH_3 or derivatives thereof which could pass through unreacted or as by-products. Suitable clean-up catalysts are available to the skilled person.

[0017] A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant reduction in volume and weight of the exhaust gas after-treatment system, in a suitable engineered system.

[0018] Several tests have been carried out in making the present invention. These are described below, and are supported by results shown in graphical form in the attached drawings.

[0019] A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

Test 1 - (Comparative)

[0020] A conventional SCR system using a commercial $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalyst, was adapted and fitted to the exhaust system of the engine. NH_3 was injected upstream of the SCR catalyst at varying ratios. The NH_3 was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of NH_3 gas to an experimental injection ring. The injection ring was a 10cm diameter annular ring provided with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow. NO_x conversions were determined by fitting a NO_x analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in Figure 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied.

[0021] A number of tests were run at different quantities of NH_3 injection, from 60% to 100% of theoretical, calculated at 1:1 NH_3/NO and 4:3 NH_3/NO_2 . It can readily be seen that at low temperatures, corresponding to light load, conversions are about 25%, and the highest conversions require stoichiometric (100%) addition of NH_3 at catalyst temperatures of from 325 to 400°C , and reach about 90%. However, we have determined that at greater than about 70% of stoichiometric NH_3 injection, NH_3 slips through the SCR catalyst unreacted, and can cause further pollution problems.

Test 2 (Comparative)

[0022] The test rig was modified by inserting into the exhaust pipe upstream of the NH_3 injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length (26.67cm diameter and 15.24cm length) containing 10g Pt/ft^3 (= 0.35g/litre) of catalyst volume. Identical tests were run, and it was observed

from the results plotted in Figure 2, that even at 225°C, the conversion of NO_x has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of NH₃ was observed in this test nor in the following test.

Test 3

[0023] The test rig was modified further, by inserting a particulate trap before the NH₃ injection point, and the tests run again under the same conditions at 100% NH₃ injection and a space velocity in the range 40,000 to 70,000 hr⁻¹ over the SCR catalyst. The results are plotted and shown in Figure 3. Surprisingly, there is a dramatic improvement in NO_x conversion, to above 90% at 225 °C, and reaching 100% at 350°C. Additionally, of course, the particulates which are the most visible pollutant from diesel engines, are also controlled.

Test 4

[0024] An R49 test with 80% NH₃ injection was carried out over a V₂O₅/WO₃/TiO₂ SCR catalyst. This gave 67% particulate, 89% HC and 87% NO_x conversion; the results are plotted in Figure 4.

[0025] Additionally tests have been carried out with a different diesel engine, and the excellent results illustrated in Test 3 and 4 above have been confirmed.

[0026] The results have been confirmed also for a non-vanadium SCR catalyst.

Claims

1. An improved SCR system for treating combustion exhaust gas containing NO_x and particulates, comprising in combination and in order, an oxidation catalyst effective to convert at least a portion of NO in said NO_x to NO₂ and enhance the NO₂ content of the exhaust gas, a particulate trap, a source of reductant fluid, injection means for such reductant fluid located downstream of said particulate trap and an SCR catalyst.
2. An SCR system according to claim 1, wherein the reductant fluid is NH₃.
3. An SCR system according to claim 1 or 2, wherein the oxidation catalyst is a platinum catalyst carried on a through-flow honeycomb support.
4. An SCR system according to claims 1, 2 or 3 wherein the particulate filter is a wall-flow filter.
5. An SCR system according to any one of the preceding claims, comprising also means to cool gases upstream of the SCR catalyst.

6. An SCR system according to claim 5, comprising also control means such that said gas cooling means is activated only when a high SCR catalyst temperature is detected or conditions are determined that are expected to lead to high catalyst temperatures.
7. A diesel engine provided with an SCR system according to any one of claims 1 to 6.
8. A light duty diesel engine according to claim 7, wherein the volume of the exhaust gas after-treatment system is reduced.
9. A method of reducing pollutants, including particulates and NO_x, in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO₂ and enhance the NO₂ content of the gas stream, removing at least a portion of said particulates in a particulate trap, reacting trapped particulate with NO₂, adding reductant fluid to the gas stream to form a gas mixture downstream of said trap, and passing the gas mixture over an SCR catalyst under NO_x reduction conditions.
10. A method according to claim 9, wherein said gas stream is the exhaust from a diesel, GDI or CNG engine.
11. A method according to claim 9 or 10, wherein the gases are cooled, if necessary, before reaching the SCR catalyst.
12. A method according to claim 9, 10 or 11, wherein the NO to NO₂ ratio in the gases is adjusted to a level pre-determined to be optimum for the SCR catalyst, by oxidation of NO over an oxidation catalyst.

Patentansprüche

1. Verbessertes System zur selektiven katalytischen Reduktion (SCR) zur Behandlung von NO_x und Feststoffteilchen enthaltendem Verbrennungsabgas, umfassend in Kombination und in dieser Reihenfolge, einen Oxydationskatalysator, der wirksam ist, um wenigstens einen Teil NO des NO_x in NO₂ umzuwandeln und den NO₂-Gehalt im Abgas zu erhöhen; ein Feinstofffilter; ein Reservoir für eine Reduktionsflüssigkeit; Einspritzvorrichtungen für eine solche Reduktionsflüssigkeit, die hinter dem Feinstofffilter angeordnet sind und einen SCR-Katalysator.
2. SCR-System nach Anspruch 1, worin die Reduktionsflüssigkeit NH₃ ist.

3. SCR-System nach Anspruch 1 oder 2, worin der Oxydationskatalysator ein auf einem Durchflusswaben­träger befindlicher Platin-Katalysator ist.
 4. SCR-System nach Anspruch 1, 2 oder 3, worin das Feinstofffilter ein Membran-Durchflussfilter ist.
 5. SCR-System nach einem der vorhergehenden Ansprüche, zusätzlich umfassend Vorrichtungen zur Kühlung von Gasen vor dem SCR-Katalysator.
 6. SCR-System nach Anspruch 5, zusätzlich umfassend Kontrolleinrichtungen, so dass die Vorrichtung zur Gaskühlung nur dann aktiviert wird, wenn eine hohe Temperatur des SCR-Katalysators festgestellt wird oder Bedingungen ermittelt werden, von denen erwartet werden kann, dass sie zu hohen Katalysatortemperaturen führen.
 7. Dieselmotor, der mit einem SCR-System nach einem der Ansprüche 1 bis 6 ausgerüstet ist.
 8. Leichter Dieselmotor nach Anspruch 7, worin das Volumen des Abgas-Nachbehandlungssystems vermindert ist.
 9. Verfahren zur Schadstoffreduzierung, welches Feinstoffe und NO_x in Gasströmen einschließt, umfassend die Überleitung eines solchen Gasstroms über einen Oxydationskatalysator unter Bedingungen, die wirksam sind, um wenigstens einen Teil NO im Gasstrom zu NO_2 umzuwandeln und den NO_2 -Gehalt des Gasstroms zu erhöhen; Entfernung wenigstens eines Teils des Feinstoffs in einem Feinstoffabscheider; Umsetzung des abgeschiedenen Feinstoffs mit NO_2 ; Zugabe von Reduktionsflüssigkeit zum Gasstrom unter Bildung eines Gasgemisches nach dem Abscheider, und Überleiten des Gasgemisches über einen SCR-Katalysator unter NO_x reduzierenden Bedingungen.
 10. Verfahren nach Anspruch 9, worin der Gasstrom das Abgas eines GDI- oder CNG-Dieselmotors ist.
 11. Verfahren nach Anspruch 9 oder 10, worin die Gase, sofern erforderlich, gekühlt werden, ehe sie den SCR-Katalysator erreichen.
 12. Verfahren nach Anspruch 9, 10 oder 11, worin das NO/NO_2 -Verhältnis in den Gasen durch Oxydation von NO über einen Oxydationskatalysator auf ein vorbestimmtes, für den SCR-Katalysator optimales Niveau, eingestellt wird.
2. Système SCR selon la revendication 1, dans lequel le fluide réducteur est du NH_3 .
 3. Système SCR selon la revendication 1 ou 2, dans lequel le catalyseur d'oxydation est un catalyseur au platine supporté sur un support en nids d'abeilles de type traversée.
 4. Système SCR selon la revendication 1, 2 ou 3, dans lequel le filtre à particules est un filtre de type traversée de paroi.
 5. Système SCR selon l'une quelconque des revendications précédentes, comprenant également des moyens pour refroidir les gaz en amont du catalyseur de réduction SCR.
 6. Système SCR selon la revendication 5, comprenant également des moyens de contrôle faisant que lesdits moyens de refroidissement des gaz ne sont activés que lorsqu'une température catalytique SCR élevée est détectée ou que des conditions susceptibles de conduire à des températures catalytiques élevées sont établies.
 7. Moteur Diesel proposé avec un système SCR selon l'une quelconque des revendications 1 à 6.
 8. Moteur Diesel léger selon la revendication 7, dans lequel le volume des gaz d'échappement après traitement est diminué.
 9. Procédé de diminution des substances polluantes, comprenant matières en suspension et NO_x , dans des flux de gaz, comprenant le fait de faire passer un tel flux de gaz sur un catalyseur d'oxydation dans des conditions efficaces pour convertir au moins une partie de NO dans le flux des gaz en NO_2 et pour augmenter la teneur en NO_2 dans le flux des gaz, d'éliminer au moins une partie desdites matières en suspension dans un piège à particules, de faire réagir la matière en suspension piégée avec NO_2 , d'ajouter un fluide réducteur au flux des gaz pour former un mélange gazeux en aval dudit piège, et de faire passer le mélange gazeux sur un catalyseur de réduction SCR dans des conditions de réduction de NO_x .

Revendications

1. Système SCR (Réduction catalytique sélective)

10. Procédé selon la revendication 9, dans lequel ledit flux des gaz correspond à l'échappement sortant d'un moteur Diesel, GDI ou GNC.
11. Procédé selon la revendication 9 ou 10, dans lequel les gaz sont refroidis, si nécessaire, avant d'atteindre le catalyseur de réduction SCR. 5
12. Procédé selon la revendication 9, 10 ou 11, dans lequel le rapport de NO à NO₂ dans les gaz est ajusté à un niveau prédéterminé pour être optimal pour le catalyseur de réduction SCR, par oxydation de NO sur un catalyseur d'oxydation. 10

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